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Simultaneous Measurements of Solute Content and Henry's Constant by Multiple Headspace Extraction Gas Chromatography

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Key Words

Gas chromatography (GC), Henry's constant, Multiple headspace extraction (MHE), Quantitative analysis by headspace, Static headspace analysis (HS).

Summary

This study presents the development of a method to simultaneously measure the contents and Henry's constants of solutes in infinitively diluted solutions using multiple headspace extraction (MHE) gas chromatography (GC). The present method is based on the assumption that the vapor-liquid equilibrium conditions are exactly repeated for each headspace extraction. We obtained a first-order linear equation that relates the sum of the measured GC peak area of the first (n-1) headspace extraction $\sum_{1}^{n-1} A^i$ to the GC peak area from the n^{th} extraction A^n. We derived the content and Henry's constant of a solute from the intercept and the slope of the linear equation, respectively, through one calibration experiment. Mathematical precision analysis indicates that the phase ratio β is the key parameter that dictates the accuracy of the method and the method is accurate over a wide range of β. Furthermore, the method is fully automated.

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Introduction

Determination of solute concentration and vapor-liquid phase equilibrium (VLE) partitioning in unknown solutions has significant practical importance in chemical and environmental engineering. There are many techniques available for quantitative analysis or VLE studies of trace species in unknown solutions. Most existing techniques, such as gas chromatography (GC), involve direct measurements of the liquid phase of the sample solution through calibration. Unfortunately, these techniques, such as direct column injection in GC analysis, are not suitable for the characterization of many industrial and environmental streams due to the corrosive nature of the samples. Tedious sample pretreatment is required in using these methods [1]. Headspace gas chromatography (HSGC) provides direct analysis of the vapor of a solute in a solution. Many measurement methods have been developed [2] using HSGC. Quantitative analysis of solute concentration can be achieved using HSGC by only measuring the vapor phase without conducting direct analysis of the liquid phase of the solution. We have developed such a method for quantitative analysis of solute in corrosive streams, i.e., weak black liquors (spent liquid from pulping) from kraft mills, using HSGC in a previous study [3]. Indirect HSGC methods have also been developed [4-7] to determine VLE partitioning coefficient, or Henry's constant, of solute without analyzing the liquid phase of the solution. In this study, we report on the simultaneous measurements of the content and the Henry's constant of a solute in an unknown sample matrix using multiple headspace extraction (MHE) gas chromatography.

The MHS gas chromatographic technique was developed in the early 1980s by Kolb [8-10]. The mathematical model of the MHE method was developed by McAuliffe [11, 12] and Suzuki et al. [13]. Later, Kolb and Ettre [14] conducted a detailed study on the theory and practice of using MHE for quantitative analysis of analyte in sample matrices. Their study was based on static headspace equilibrium between the liquid and the vapor phases and the repeated equilibrium conditions in each headspace extraction. They concluded that the MHE procedure is very similar to dynamic gas extraction (or the purge and trap), but is carried out stepwise. Therefore, the total peak area extrapolated from the sum of the peak areas measured from each extraction is proportional to the total mass of the analyte in the original sample. The proportional constant can be obtained through one calibration

experiment. The present study uses the same physical basis proposed by Kolb and Ettre [14] to develop a MHE GC method for simultaneous measurements of the content and Henry's constant of a solute. The method is rapid, automated, and accurate. More importantly, it simultaneously provides two key parameters of an unknown solution through only one measurement.

Methodology

When a sample solution of volume V_1 with a solute mass of m_0 is introduced into a closed vial of volume V_T, some of the solute may be transported from the liquid phase through the liquid-gas interface into the gas phase to become vapor, while some of the vapor may diffuse into the solution at the interface. These two mass transport processes will reach a dynamic equilibrium between the vapor and liquid phases after some time. The equilibrium pressure in the headspace is P_o. At equilibrium, the concentration of the solute in the vapor phase C_g is proportional to the concentration of the solute in the liquid phase C_l. For infinitively diluted solutions, the proportionality coefficient is the dimensionless Henry's constant H_c of the solute, i.e.,

$$H_c = \frac{C_g}{C_l}, \tag{1}$$

where C_g and C_l are volumetric concentration, e.g., mol/L or mg/L.

Pressurization of the sample vial to a pressure of $P_h(0)$ using inert gas is a common practice in headspace measurements to create a pressure head for sampling at vapor-liquid phase equilibrium. It is often assumed that the pressurization time is very short so that the equilibrium remains unchanged. It should be pointed out that the solute volumetric concentration C_g within the headspace is a constant before and after pressurization. After pressurization, the headspace vapor is vented out to fill the sample loop. The sample is then injected into the GC column to complete the first headpsace measurement. Further venting is often necessary to reduce the headspace pressure close to its initial equilibrium pressure P_o. The headspace measurement disturbed the equilibrium in the vial. According to Kolb and Ettre [14], a new VLE can be reestablished within the vial after a while and the VLE

conditions are exactly repeated. We can conduct another headspace measurement. This procedure can be repeated several times. We label each equilibrium state as *1, 2, ..., i, ..., n*, correspondingly, in the following derivation of the present MHE method.

The initial mass of the solute m_1 (or the solute mass at the first equilibrium state) in the sample vial can be expressed as:

$$m_1 = C_g^1 V_g + C_l^1 V_l, \tag{2}$$

where V_g and V_l are the volumes of vapor and liquid phases in the vial, respectively.

Each headspace measurement extracts certain a amount of solute vapor out of the headspace in the sample vial. We can express the volumetric flow out of the headspace as a certain percentage of the total headspace gas volume at pressurization pressure $P_h(0)$, i.e., $\varphi \cdot V_g$. Then the mass flow out of the headspace is equal to the volumetric flow times the solute equilibrium volumetric concentration C_g (a constant before and after pressurization), i.e., $C_g \cdot \varphi \cdot V_g$. Therefore, the total mass of the solute within the vial after the first headpsace measurement is reduced to m_2, i.e.,

$$m_2 = (C_g^2 V_g + C_l^2 V_l) = m_1 - \varphi C_g^1 V_g, \tag{3}$$

where $\varphi<1$ is called the volumetric flow coefficient and can be derived from basic fluid mechanics knowledge.

At the second equilibrium state, all the VLE conditions are exactly repeated. Furthermore, the second headspace extraction is exactly the same as the first one. Therefore, the volumetric flow out of the headspace should be the same. More specifically, the volumetric flow coefficient φ is a constant, though the absolute solute mass extracted is reduced due to the reduced solute concentrations of the liquid and vapor phases within the vial. We will calculate and verify φ in the Appendix from fluid mechanics using the mechanical energy equation. We can apply φ to all the headspace extractions conducted later. Therefore, we have

$$m_3 = (C_g^3 V_g + C_l^3 V_l) = m_2 - \varphi C_g^2 V_g = m_1 - \varphi V_g (C_g^1 + C_g^2), \quad (4)$$

$$\vdots$$

$$\vdots$$

$$m_n = (C_g^n V_g + C_l^n V_l) = m_1 - \varphi V_g (C_g^1 + C_g^2 + \cdots + C_g^{n-1}) = m_1 - \varphi V_g \sum_1^{n-1} C_g^i . \quad (5)$$

We neglected the change of solute volume V_1 due to heating and headspace extraction in the above derivation.

For infinitively diluted solutions, the equilibrium concentration ratio of the vapor phase over the liquid phase is equal to Henry's constant of the solute, i.e.,

$$H_c = \frac{C_g^1}{C_l^1} = \frac{C_g^2}{C_l^2} = \frac{C_g^3}{C_l^3} = \cdots = \frac{C_g^n}{C_l^n}. \quad (6)$$

Substituting Eqn. (6) into Eqn. (5), we have

$$C_g^n \left(V_g + \frac{V_l}{H_c} \right) = m_1 - \varphi V_g \sum_1^{n-1} C_g^i \ . \quad (7)$$

If gas chromatography is used for the MHE analysis, the GC response measured as the peak area A is proportional to the solute concentration in the headspace C_g., i.e.,

$$A = kC_g, \quad (8)$$

where k is a proportionality constant. Substituting Eqn. (8) into Eqn. (7), we have

$$\sum_1^{n-1} A^i = \frac{k \cdot m_1}{\varphi V_g} - \frac{A^n}{\varphi} \left(1 + \frac{1}{H_c} \cdot \frac{V_l}{V_g} \right). \quad (9)$$

We can rewrite Eqn. (9) as a first-order linear equation,

$$\sum_1^{n-1} A^i = a + bA^n , \quad (10)$$

with

$$a = \frac{k \cdot m_1}{\varphi V_g}, \tag{11}$$

and

$$b = -\frac{1}{\varphi}\left(1 + \frac{1}{H_c} \cdot \frac{V_l}{V_g}\right) = -\frac{1}{\varphi}\left(1 + \frac{1}{\beta \cdot H_c}\right), \tag{12}$$

where $\beta = \frac{V_g}{V_l}$ is the phase ratio according to Kolb and Ettre [14].

We can obtain $\sum_{1}^{n-1} A^i$ and A^n through MHE GC measurements. We then can conduct a linear regression analysis to obtain the intercept a and the slope b of Eqn. (10). The concentration and the Henry's constant of the solute can be calculated from a and b using Eqns. (11) and (12), i.e.,

$$C_0 = \frac{m_1}{V_l} = \frac{a\varphi}{k} \cdot \frac{V_g}{V_l} = \frac{a\varphi}{k}\beta, \tag{13}$$

and

$$H_c = -\frac{1}{(1+\varphi b)\beta}. \tag{14}$$

where k and φ are two unknown constants and can be determined from calibration experiments.

Experimental

Chemicals

Methanol, ethanol, and isopropanol of analytical grade were used as solutes and de-ionized water as solvent to prepare methanol-, ethanol-, and isopropanol-water solutions.

The methanol-water solution was used as standard solution for calibration to obtain k and φ with a known methanol concentration of 800 mg/L and Henry's constant at a temperature range of 25-80°C from literature [16-20] and our previous study [7].

Apparatus and Operation

All measurements were carried out using a HP-7694 Automatic Headspace Sampler and HP-6890 capillary gas chromatography (Hewlett-Packard, Palo Alto, CA, U.S.A.) equipped with a HP ChemStation for data acquision and analysis. The operation of the headspace sampler has been described in our previous study [3]. The basic operating principles and procedures of the headspace sampler for multiple headspace extraction are very similar to that described by Kolb and Ettre [14], except that the venting process was combined with the sample transfer process in the present headspace sampler. More specifically the sample loop is open to atmosphere during sample transfer. The duration of the sample transfer process (sample loop fill time) controls the pressure inside the sample vial. Headspace operating conditions: compressed air is used for vial pressurization. The pressurization time of the Headspace Sampler: 0.2 min, sample loop fill time: 1.0 min., and loop equilibration time: 0.05 min. GC conditions: HP-5 capillary column at 30°C; carrier gas helium flow (He): 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively.

The measurement procedure was as follows: pipette 50 μl of sample solution into a 20-mL vial, which gives a phase ratio β=399, then close the vial and put it into the Headspace Sampler. The sample size (or β) can be varied as necessary. The Headspace Sampler then heats the sample in the vial to a desired temperature with strong shaking for three minutes to achieve vapor-liquid equilibrium within the vial. At equilibrium, the vial is pressurized by compressed air, and the headspace is partially withdrawn for sample transfer and venting to the atmosphere to reduce the vial pressure to its initial vial pressure. The sample is injected into the GC column for analysis. The GC signal as peak area A is recorded. This procedure is repeated 10 times for multiple headspace extraction analysis automatically and can be programmed from the HP ChemStation.

Method Calibration

Determination of Volumetric Flow Coefficient φ

The volumetric flow coefficient φ relates the solute Henry's constant H_c to the slope of Eqn. (10) b, a measurable quantity (b is a function of peak area A according to Eqn. (10)) through Eqn. (14). As shown in the Appendix, φ is independent of solute, solvent, and solution systems, and is dependent on the headspace operating parameters, such as temperature, pressure, sample loop fill time, phase ratio β, etc. Therefore, φ can be obtained through calibration using a solution with known solute Henry's constants at different temperatures using Eqn. (14).

We conducted multiple headspace extraction measurements in a methanol-water solution of concentration 800 mg/L at temperatures 40, 50, 60, 70, and 80°C to calibrate the volumetric flow coefficient φ. The Henry's constants of methanol at these temperatures shown in Table I are obtained from literature [16-20] and our previous study [7]. The MHE experiments were carried out at a phase ratio β=399. Linear regressions of the GC peak areas were conducted according to Eqn. (10) to obtain b's. The results are shown in Fig. 1 and Table I. We also obtained the calibration constant k using the intercept a's and φ's through Eqn. (13) from this set of experiments as shown in Table I. We then conducted a linear regression analysis to correlate φ with temperature T in °C. We can apply the following regression equation of φ to any solute-solution systems as long as the HSGC operating conditions remain the same.

$$\varphi(\beta=399) = 0.3776 - 0.0057 \cdot T + 7.7613 \times 10^{-5} \cdot T^2 \qquad (15)$$

If the phase ratio β changes or the headspace volume V_g changes, the following equation derived from the relation of φ and headspace volume V_g as listed in the Appendix can be used to correct the effect of β on the volumetric flow coefficient φ. As long as the pressure in the sample vial after pressurization $P_h(0)$ remains the same.

$$\varphi(\beta) = \frac{\beta_{cal}}{\beta_{cal}+1}\frac{\beta+1}{\beta}\varphi(\beta_{cal}) = \frac{399}{400}\cdot\frac{\beta+1}{\beta}\cdot\varphi(\beta=399) \qquad (16)$$

Determination of Concentration Calibration Constant *k*

The constant k relates the measured GC peak area A to the solute vapor concentration C_g in the headspace sampler through Eqn. (8). In direct headspace GC analysis, k is obtained through calibration experiments using vapor [15] or gas samples. However, it should be pointed out that k also relates the solute concentration in original sample C_o to a GC measurable quantity a (a function of GC peak area A according to Eqn. (10)) through Eqn. (13). Therefore, we can determine k through calibration experiments using liquid samples according to Eqn. (13), which greatly simplifies the calibration because any calibration that involves vapor and gas is always difficult. It should be pointed out that k is only dependent on the solute not the solvent and the solution system. Therefore, calibration can be carried out using a simple binary solution of the solute to be analyzed.

We have obtained the calibration constant k from the calibration experiments for φ. To obtain more precise calibration of k, we conducted multiple headspace extraction measurements using five methanol-water solutions of concentrations of 400, 800, 1200, 1600, and 2000 mg/L at headspace temperature 70°C. We conducted linear regressions of the measured GC peak areas according to Eqn. (10) to obtain the incept a's and slope b's of Eqn. (10). We calculated the concentration calibration constant k according to Eqn. (13) using the a's obtained and φ calculated from Eqn. (15). The results are listed in Table II. The average value of k=353.1 was used in this study. The relative standard deviation of 1.3% was used as a reference to determine the relative variance $\sigma^2(k)$ for precision analysis. We used the values of the slope b's from the regressions to calculate back the volumetric flow coefficient φ for these five (5) MHE experiments as listed in Table II. We then can calculate the relative standard deviation of φ=1.8% that was used as a reference to determine the relative variance $\sigma^2(\varphi)$ in precision analysis. Each regression gave a relative standard deviation of a and b. The averaged relative standard deviations of a and b 1.0 and 1.7%, respectively, and were used to determine the relative variances $\sigma^2(a)$ and $\sigma^2(b)$ in precision analysis.

Results and Discussions

Precision Analysis of the Method

We conducted a mathematical precision analysis of the present MHE GC method for simultaneous determination of the content of and the Henry's constant of a solute by Eqns. (13) and (14) using the following variance estimation Eqns., respectively,

$$\sigma^2(C_0)=\left(\frac{\partial C_0}{\partial a}\right)^2\sigma^2(a)+\left(\frac{\partial C_0}{\partial k}\right)^2\sigma^2(k)+\left(\frac{\partial C_0}{\partial \varphi}\right)^2\sigma^2(\varphi)+\left(\frac{\partial C_0}{\partial \beta}\right)^2\sigma^2(\beta) \quad (17)$$

$$\sigma^2(H_c)=\left(\frac{\partial H_c}{\partial b}\right)^2\sigma^2(b)+\left(\frac{\partial H_c}{\partial \varphi}\right)^2\sigma^2(\varphi)+\left(\frac{\partial H_c}{\partial \beta}\right)^2\sigma^2(\beta) \quad (18)$$

where the variances $\sigma^2(k)=2.0\%k^2$, $\sigma^2(\varphi)=2.0\%\varphi^2$, $\sigma^2(a)=2.0\%a^2$, and $\sigma^2(b)=2.0\%b^2$ are determined based on experimentally measured relative standard deviations of k(1.3%), φ(1.8%), a(1.0%), and b(1.7%), respectively, during calibration experiments as discussed above. The variance of phase ratio $\sigma^2(\beta)$ is calculated from the variances of the phase volumes $\sigma^2(V_g)$ and $\sigma^2(V_l)$ similar to Eqns. (17) and (18) as follows:

$$\sigma^2(\beta)=\frac{1}{V_l^2}\sigma^2(V_g)+\frac{V_g^2}{V_l^4}\sigma^2(V_l) \quad (19)$$

where $\sigma^2(V_g)=1.0\%V_g^2$ and $\sigma^2(V_l)=1.0\%V_l^2$ were determined based on experimentally obtained standard deviations of the phase volumes. Therefore, we have $\sigma^2(\beta)=2\text{x}(1.0\%\beta)^2=2.0\text{x}10^{-4}\beta^2$ from Eqn. (19).

We wrote a PC-based C-program to carry out the mathematical uncertainty calculations using Eqns. (17) and (18). We found that the phase ratio β is a key parameter that controls the accuracy of the present MHE method. Figure 2 shows the effect of β on the measurement uncertainty of solute concentration C_0. The results indicate that a β value of greater than 2 is required to obtain good measurements of solute concentration with uncertainties less than 10%. Figure 3 shows the effect of β on the measurement uncertainty of solute Henry's constant in solutions. Equation (16) was used to account the effect of phase ratio β on the volumetric flow coefficient φ. The results indicate that the

measurement uncertainty is also affected by the solute Henry's constant in the solution. For a giving solute-solvent system or a giving solute Henry's constant, there is an optimum β value at which the uncertainty is minimum. Furthermore, when the Henry's constant increases, the optimum β value decreases and the minimum uncertainty increases as shown in Fig. 4. In other words, a small β is necessary to measure a large Henry's constant. Figure 4 also plotted the β boundary within which the measurement uncertainty is less than 10% as a guideline for experiments. The results in Figs. 2 and 4 suggest that a minimum $\beta = 3$ is recommended for simultaneous measurements of solute content and Henry's constant using the present MHE method. Furthermore, the precision analysis indicates that a phase ratio β around 5 can give good measurements of solute Henry's constant in a wide range (H_c<1.0). Although the method is applicable to measure solute content in any system, it is not suitable to measure Henry's constant >1.0. We also found that increasing the volume of the sample vial V_T does not affect the above uncertainty characteristics, but shifts the optimum phase ratio β to a greater value.

The Pressure in the Headspace

The pressure in the headspace during vapor-liquid phase equilibrium is controlled at approximately one atmosphere (1 atm) through venting to atmosphere. Because the sample was taken at room temperature initially and added into a sample vial that was heated later to obtain a desired temperature, the pressure in the headspace at the first equilibrium state is somewhat higher than one atmosphere caused by the expansion of air in the vial due to heating. Thus, a lower signal is expected as shown in Fig. 5. Therefore, we exclude the first data point in regression analysis of the peak areas using Eqn. (10). For many applications, the liquid-vapor phase equilibrium data at different pressures are desirable. By properly controlling the pressure in the sample vial during venting, the present method can be used to measure Henry's constant at different pressures. Furthermore, the pressurization pressure also dictates the volumetric ratio coefficient φ. Unfortunately, most commercial headspace gas chromatographic systems do not provide a control of the pressurization pressure rather than the pressurization time, which is a significant limitation of most commercial headspace GC systems.

Method Validation

Repeatbility Test of Multiple Headspace Extraction

According to the derivation by Kolb and Ettre [14], the Logarithmic peak area obtained from the *i*th headspace extraction $Log(A^i)$ should be linearly proportional to (i-1) or simply the extraction number i if the VLE conditions for each headspace extraction can be exactly repeated in MHE measurements. We plot the GC signal of peak area A^i of methanol measured in a methanol–water solution of concentration 800 mg/L at temperature 60°C. We obtained a near perfect linear correlation with a correlation coefficient of 0.9994 between the peak area A^i and the extraction number i as shown in Fig. 5, indicating the validity of the basic assumption that the VLE conditions were exactly repeated for each headspace extraction measurement in this study. We then carried out a linear regression analysis according to Eqn. (10) to test the accuracy of the experiment. Again, we obtained a near perfection regression as shown in Fig. 6 with a correlation coefficient of 0.9997. With such a good correlation, we are confident that the concentration and the Henry's constant derived from the intercept a and the slope b of the regression analysis, respectively, will be accurate. It should be pointed out that a minimum of three extractions excluding the first extraction is required to use the present MHE method through Eqn. (10).

Solute Content Measurement

We conducted comparison measurements of methanol concentrations in nine environmental samples collected from a kraft pulp mill to validate the present MHE GC method. Methanol contents were measured by both the present MHE method and an indirect HSGC method that we developed in a previous study [3]. The results obtained by these two methods agree very well as shown in Table III, indicating the validity of the present method for solute content measurements in any solute-solvent solutions.

Henry's Constant Measurement

We measured the Henry's constants of isopropanol and ethanol in water solutions at a temperature range of 40-80°C using the present MHE GC method. We compared our measurements to those obtained by Kolb et al. [15]. Linear regression shows that the Logarithm fits to the Henry's constants of isopropanol and ethanol, respectively, reported by

Kolb et al. [15] and those measured by the present MHE method very well as shown in Fig. 7. Correlation coefficients of 0.9999 and 0.9984 were obtained from the fitting of the two sets of data of isopropanol and ethanol to the inverse of temperature in Kelvin, respectively, demonstrating the validity and the accuracy of the present method for the measurements of solute Henry's constant.

Conclusion

We developed a multiple headspace extraction (MHE) technique for simultaneous measurements of contents and Henry's constants of solutes in infinitively diluted solutions using a commercial headspace gas chromatograph. Mathematical precision analysis of the method indicates that the phase ratio β is a key factor that dictates that accuracy of the method and the method is very accurate for measurements of solute contents and Henry's constants in a wide range of β. The methanol concentrations measured using the present method in several environmental samples from a kraft pulp mill agree with those measured by an indirect HSGC method very well. The measured Henry's constants of isopropanol and ethanol in water solutions are in excellent agreement with those in the literature. The present method is very simple, efficient, and fully automated. It can be easily applied to any environmental and industrial samples with complicated matrices.

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Fig. 1

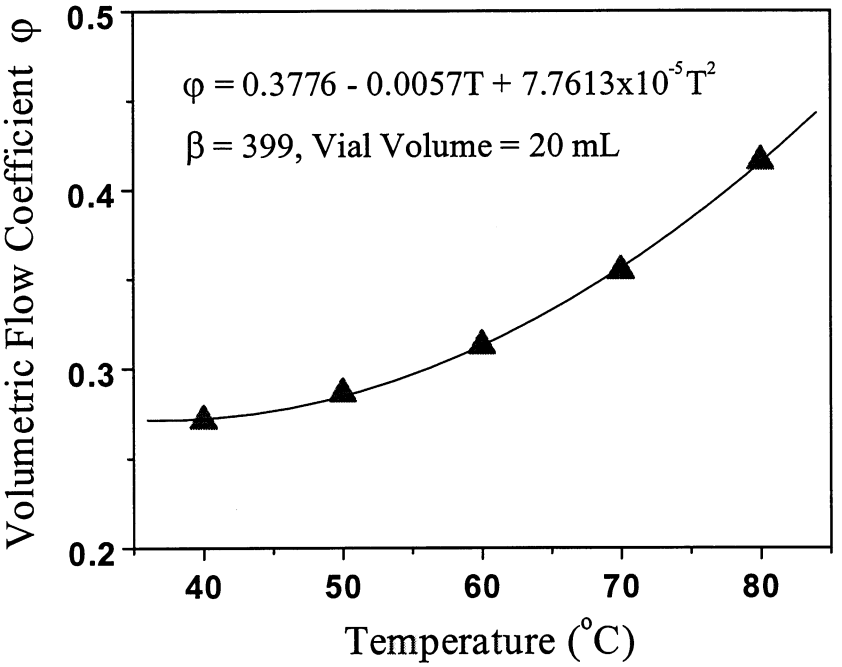
Volumetric Flow Coefficient φ
0.5
0.4
0.3
0.2
φ = 0.3776 - 0.0057T + 7.7613x10^-5 T^2
β = 399, Vial Volume = 20 mL
40
50
60
70
80
Temperature (°C)

Fig. 2

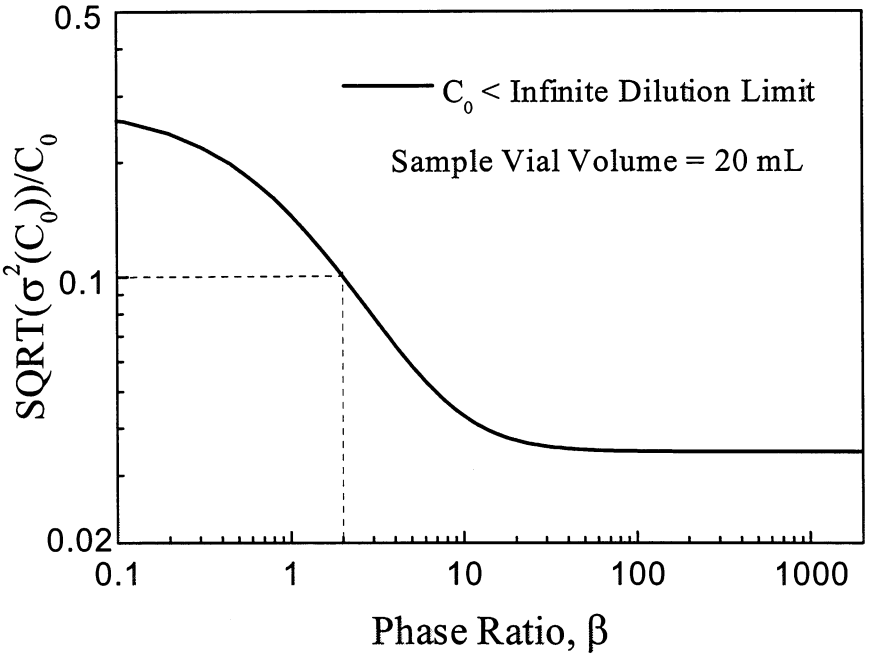
SQRT(σ^2(C0))/C0
0.5
0.1
0.02
C0 < Infinite Dilution Limit
Sample Vial Volume = 20 mL
0.1
1
10
100
1000
Phase Ratio, β

Fig. 3

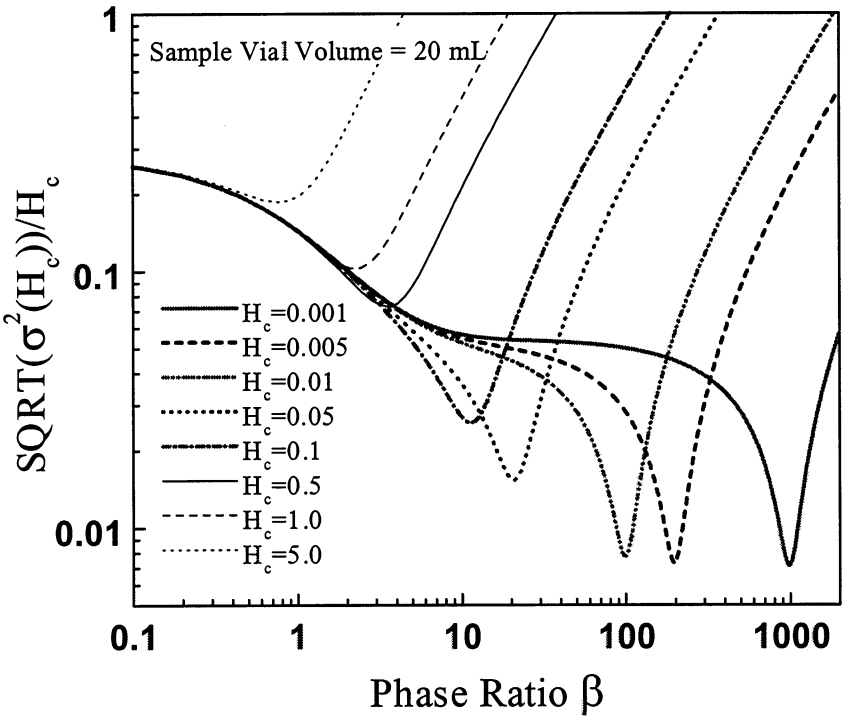
Sample Vial Volume = 20 mL
SQRT(σ²(Hc))/Hc
Phase Ratio β
Hc=0.001
Hc=0.005
Hc=0.01
Hc=0.05
Hc=0.1
Hc=0.5
Hc=1.0
Hc=5.0
1
0.1
0.01
0.1
1
10
100
1000

Fig. 4

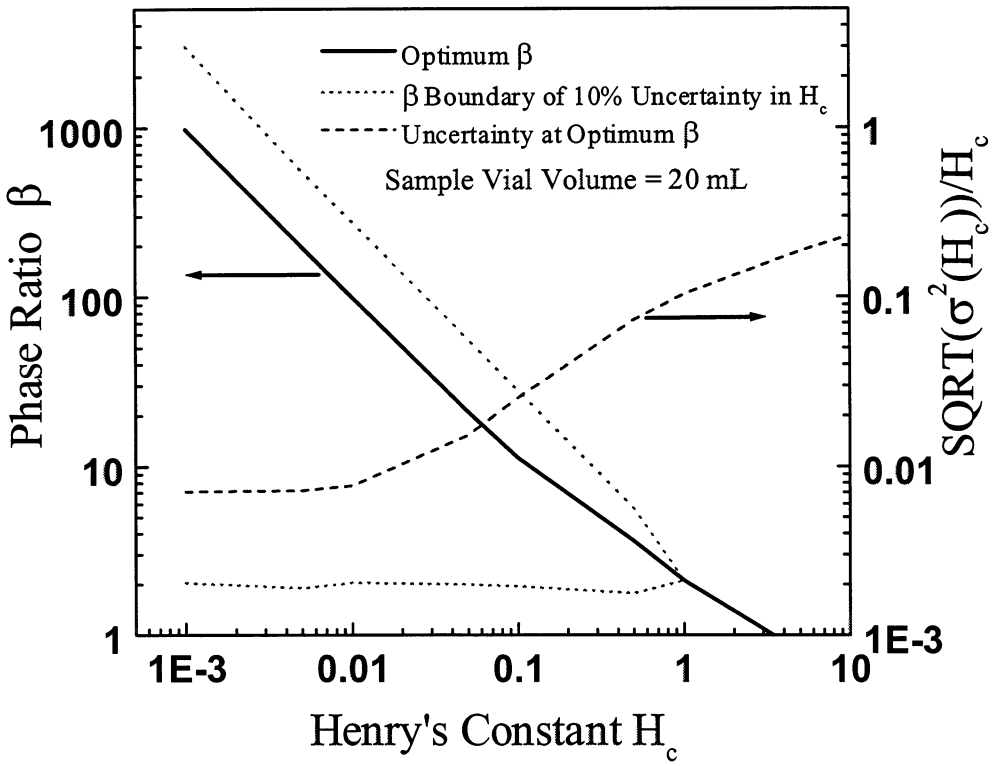
Optimum β
β Boundary of 10% Uncertainty in Hc
Uncertainty at Optimum β
Sample Vial Volume = 20 mL
Phase Ratio β
SQRT(σ²(Hc))/Hc
Henry's Constant Hc
1000
100
10
1
1
0.1
0.01
1E-3
1E-3
0.01
0.1
1
10

Fig. 5

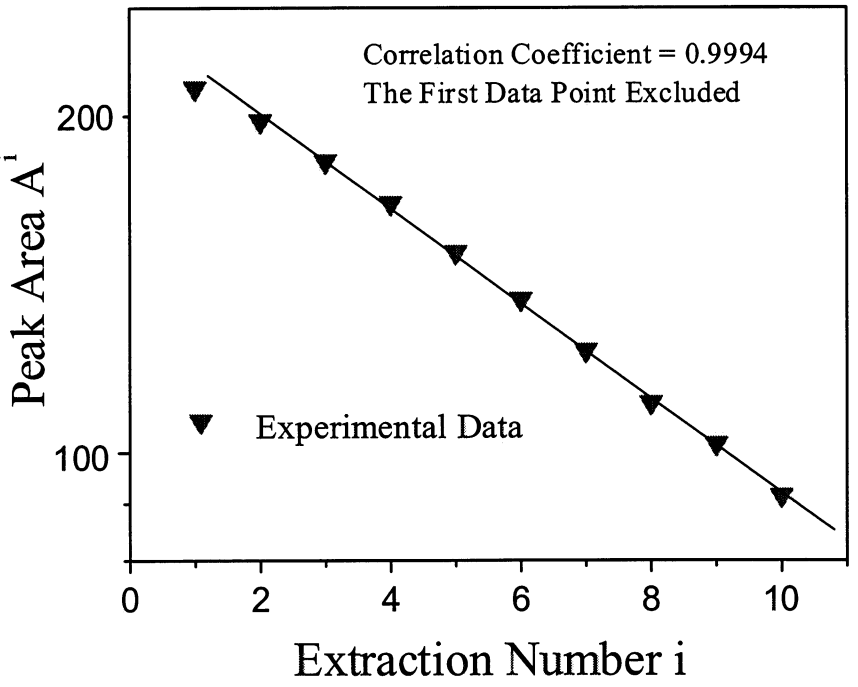
Correlation Coefficient = 0.9994
The First Data Point Excluded
Experimental Data
Peak Area A^i
Extraction Number i
200
100
0
2
4
6
8
10

Fig. 6

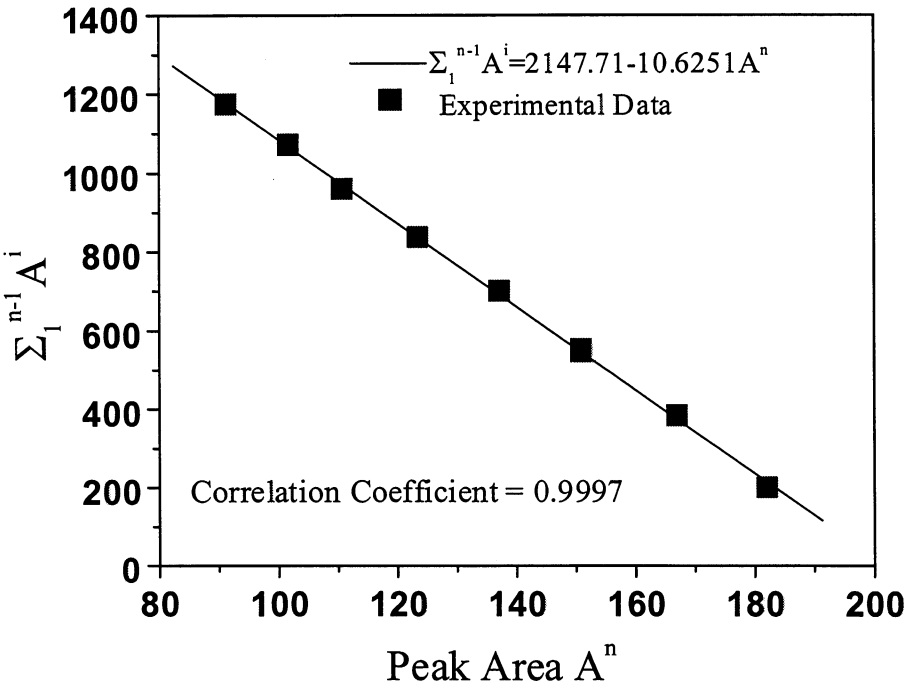
$\Sigma_1^{n-1}A^i=2147.71-10.6251A^n$
Experimental Data
Correlation Coefficient = 0.9997
$\Sigma_1^{n-1}A^i$
Peak Area A^n
1400
1200
1000
800
600
400
200
0
80
100
120
140
160
180
200

Fig. 7

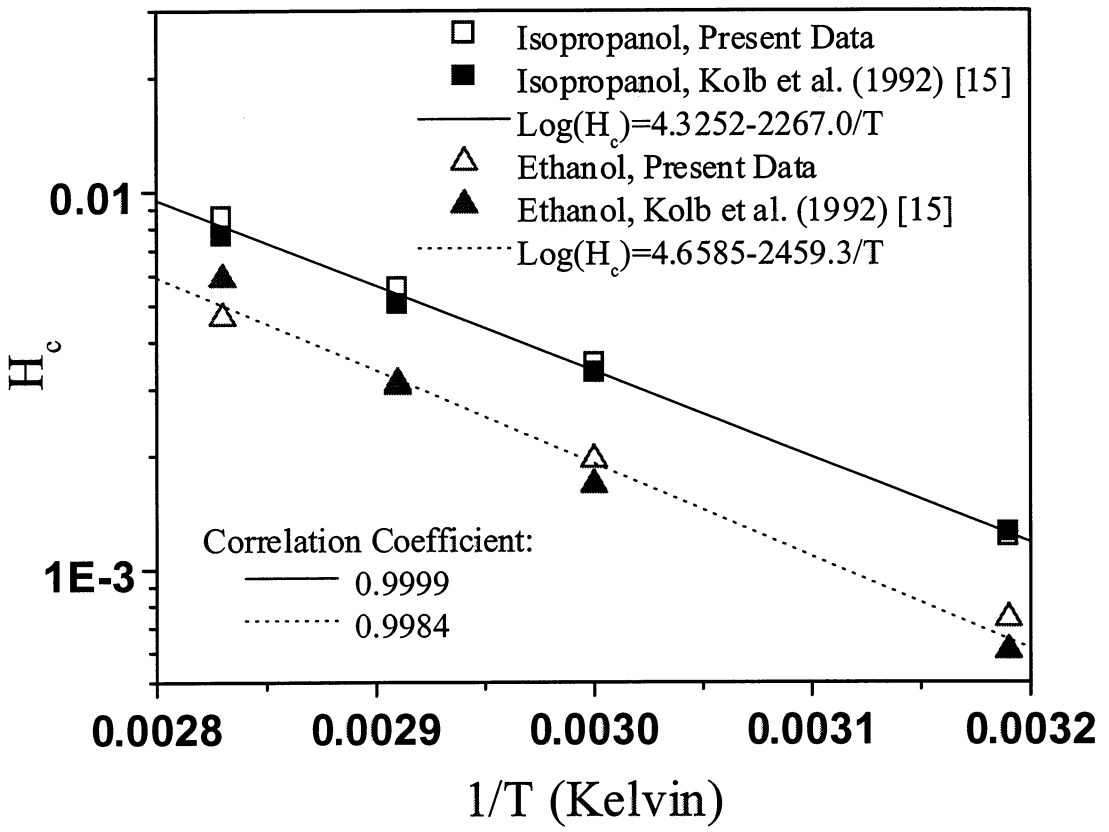
Isopropanol, Present Data
Isopropanol, Kolb et al. (1992) [15]
Log(H_c)=4.3252-2267.0/T
Ethanol, Present Data
Ethanol, Kolb et al. (1992) [15]
Log(H_c)=4.6585-2459.3/T
Correlation Coefficient:
0.9999
0.9984
0.01
1E-3
H_c
0.0028
0.0029
0.0030
0.0031
0.0032
1/T (Kelvin)

Table I

Temperature (°C)	**Given Henry's Constant H_c**	**Regression b**	**Calibrated φ**	**Regression a**	**Calibrated k**
40	0.00044	-23.12 ± 0.41	0.271	3205 ± 36	468
50	0.00071	-14.92 ± 0.12	0.286	2815 ± 14	433
60	0.00112	-9.83 ± 0.13	0.313	2496 ± 15	420
70	0.00170	-6.61 ± 0.12	0.354	1849 ± 18	353
80	0.00260	-4.55 ± 0.06	0.416	1352 ± 10	303
Relative Standard Deviation (RSTD)	N/A	1.4%	N/A	0.8%	N/A

Table II

Sample No.	**Content (mg/L)**	**Regression a**	**Calibrated k**	**Regression b**	**Calibrated φ**	**Measured H_cx1000**
1	400	925 ± 12	350	-6.80 ± 0.11	0.347	1.756
2	800	1848 ± 21	350	-6.61 ± 0.14	0.357	1.755
3	1200	2825 ± 24	356	-6.58 ± 0.13	0.359	1.771
4	1600	3707 ± 26	351	-6.44 ± 0.07	0.367	1.741
5	2000	4754 ± 53	360	-6.68 ± 0.10	0.354	1.725
Mean		N/A	353	-6.62	0.357	1.750
Relative Standard Deviation (RSTD)		1.0%	1.3%	1.7%	1.8%	0.9%

Table III

Sample No.	Methanol concentration (mg/L)		Relative Difference (%)
	The previous method [3]	The present method	
1	53	52	-1.9
2	94	91	-3.2
3	183	183	0.0
4	311	331	6.4
5	402	390	-2.3
6	613	605	-1.0
7	678	700	3.2
8	775	808	4.3
9	969	992	2.4

APPENDIX: Volumetric Flow Coefficient φ

The volumetric coefficient φ is defined as the total volumetric flow from the headspace to the sample loop and partially vented to the atmosphere during the sample transfer process at pressurization pressure $P_h(0)$ divided by the gas volume in the headspace at the same pressure, i.e.,

$$\varphi = \frac{Q_{Ph(0)}}{V_g}. \tag{A1}$$

We can calculate volumetric flowrate $\dot{Q}$ from the velocity and the cross-sectional area of the transfer line through integration,

$$\dot{Q}(t) = \int_0^t (\vec{V}(t) \cdot \vec{n}) \cdot dS = \overline{V}(t) \cdot S, \tag{A2}$$

where $\vec{V}(t)$ and $\overline{V}(t)$ are the instantaneous velocity vector and the average velocity of the flow in the transfer line, respectively, and S is the cross-sectional area of the transfer line. $\vec{n}$ is the surface normal vector of S. We can obtain the total volumetric flow by integrating the flowrate using the following equation:

$$Q = \int_0^{t^*} \dot{Q}(t) dt = \int_0^{t^*} [(\overline{V}(t) \cdot S] dt, \tag{A3}$$

where t^* is the total duration time of the venting process provided that $P(t^*) = P_o$.

We can determine the average flow velocity $\overline{V}(t)$ using the mechanical energy equation (or the modified Bernoulli equation) from fluid mechanics [A1]. For the flow from the vial headspace (station h) to the end of the sample loop or atmosphere (station a), we can assume that the headspace gas temperature T_h does not change during sample transfer and the temperature of the transfer line is held constant during the entire experiment; therefore, the thermal energy input $Q(T)$ from the heating of the transfer line is a function of the headspace gas temperature only. Furthermore, we can neglect the energy loss by friction. There is no mechanical energy input. So, we can express the mechanical energy equation as:

$$(C_v T_a + \frac{P_a}{\rho} + \frac{\overline{V}_a^2(t)}{2} + gZ_a) - (C_v T_h + \frac{P_h(t)}{\rho} + \frac{\overline{V}_h^2(t)}{2} + gZ_h) = Q(T_h), \tag{A4}$$

where C_v is the constant volume specific heat; P is pressure; ρ is gas density; g is gravitational acceleration; and Z is the vertical height of the flow. At station h (within the headspace), the flow velocity is close to zero from continuity equation (mass conservation) because the flow area is much larger than that of the transfer line, i.e, $V_h(t)=0$. And the gas density can be calculated using the ideal gas law: $\rho=P/RT$. We can find the average flow velocity $V(t)$ from Eqn. (A4),

$$\overline{V}(t)=\overline{V}_a(t)=\sqrt{2Q(T_h)+2C_v[T_h-T_a]+2[P_h(t)-P_a]\cdot\frac{RT_h}{P_h(0)}+2g(Z_h-Z_a)}\,. \quad \text{(A5)}$$

Substituting Eqn. (A5) into Eqn. (A3), we can obtain the volumetric flow out of the headspace at pressure P_a,

$$Q=\sqrt{2}\int_0^{t^*}\left\{\sqrt{q(t)+C_v[T_h-T_a]+[P_h(t)-P_a]\cdot\frac{RT_h}{P_h(0)}+g(Z_h-Z_a)}\cdot S\right\}dt\,. \quad \text{(A6)}$$

where R is gas constant and is dependent on the gases within the headspace.

The equivalent volumetric flow $Q_{ph(0)}$ at pressure $P_h(0)$ and temperature T_h can be calculated from Q using the following equation,

$$Q_{ph(0)}=\frac{P_a\cdot T_h}{P_h(0)\cdot T_a}\cdot Q\,. \quad \text{(A7)}$$

Substituting Eqn. (A7) into Eqn. (A1), we have

$$\varphi=\frac{\sqrt{2}}{V_g}\frac{P_a\cdot T_h}{P_h(0)\cdot T_a}\int_0^{t^*}\left\{\sqrt{q(t)+C_v[T_h-T_a]+[P_h(t)-P_a]\cdot\frac{RT_h}{P_h(0)}+g(Z_h-Z_a)}\cdot S\right\}dt \quad \text{(A8)}$$

where V_g can be substituted with phase ratio β and the sample vial volume V_T, we have

$$\varphi=\frac{\sqrt{2}}{V_T}\frac{\beta+1}{\beta}\frac{P_a\cdot T_h}{P_h(0)\cdot T_a}\int_0^{t^*}\left\{\sqrt{q(t)+C_v[T_h-T_a]+[P_h(t)-P_a]\cdot\frac{RT_h}{P_h(0)}+g(Z_h-Z_a)}\cdot S\right\}dt$$

Eqn. (A8) indicates that φ is a function of the gas constant R, headspace temperature T_h, and pressure $P_h(0)$, P_o. However, we know that compressed air accounts for the majority of the headspace gases in analyzing infinitively diluted solutions. Therefore, R can be treated as independent of the solute-solvent system. The rest of the parameters in Eqn. (A6) are only dependent on the experimental headspace conditions. We can calibrate φ for a

given experimental condition using a solution system with known solute Henry's constant at a desired temperature range for given experimental conditions.

Reference:

A1. *B.R. Munson, D.F., Young, T.H. Okiishi,* Fundamentals of Fluid Mechanics, 2nd Ed., John Wiley & Sons, Inc., New York, 1994, p. 268.